

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

THIS PAGE BLANK (USPTO)

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C08F 297/04, C09J 153/02 C09D 153/02, C08G 81/02	A1	(11) International Publication Number: WO 93/24547 (43) International Publication Date: 9 December 1993 (09.12.93)
--	----	---

(21) International Application Number: PCT/EP93/01407 (22) International Filing Date: 3 June 1993 (03.06.93) (30) Priority data: 92201623.3 4 June 1992 (04.06.92) EP (34) Countries for which the regional or international application was filed: AT et al. (71) Applicant (for CA only): SHELL CANADA LIMITED [CA/CA]; 400 - 4th Avenue S.W., Calgary, Alberta T2P 2H5 (CA). (71) Applicant (for all designated States except CA): SHELL IN- TERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).	(72) Inventors: DEBIER, Eric, Rene, Suzanne ; Avenue Jean Monnet 1, B-1348 Ottignies Louvain-La-Neuve (BE). DUPONT, Martine, Jeanne ; Avenue Jean-Monnet 1, B- 1348 Ottignies Louvain-La-Neuve (BE). (81) Designated States: AU, BR, CA, FI, JP, KR, NO, RU, Eu- ropean patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report.
--	--

(54) Title: VINYLAROMATIC BLOCK COPOLYMERS BEING HIGHLY SENSITIVE TO RADIATION CURING AND COMPOSITIONS CONTAINING THEM

(57) Abstract

Radiation sensitive block copolymers $(AB)_p(B)_qX$ wherein A is a poly(vinylaromatic) block and B is a poly(butadiene) block, wherein X is the residue of a polyvalent coupling agent, wherein p has a number average value of at least 1.5 and wherein q has a number average value of 0 or higher, whereas the sum of p and q values being at least 4, the block copolymer having an average bound vinylaromatic content in the range of from 7 to 35 wt. % and having a total apparent molecular weight in the range of from 50,000 to 1,500,000, and wherein the vinyl content in the poly(butadiene) blocks is in the range of from 35 to 70 %; radiation curable sealing, coating or adhesive compositions comprising said block copolymers, a process for their preparation and pressure sensitive curable tapes or labels derived therefrom.

VINYLAROMATIC BLOCK COPOLYMERS BEING HIGHLY SENSITIVE TO
RADIATION CURING AND COMPOSITIONS CONTAINING THEM

The invention relates to block copolymers, containing at least one block predominantly derived from a vinylaromatic monomer and at least one block predominantly derived from a conjugated diene, and more particularly to block copolymers which have shown an attractive sensitivity to radiation curing and to radiation curable sealant, coating and/or adhesive compositions containing said block copolymers.

More in particular the invention is relating to pressure sensitive adhesive compositions containing these block copolymers and providing attractive high temperature resistance even after low radiation dosages, whereas the tack properties remain unchanged.

From the middle seventies several efforts were made to come to block copolymers giving improved properties to adhesive compositions which should be economically processed into their end user form, i.e. giving an optimum balance between processing speed (throughput) and final adhesive properties.

Such efforts can be derived from e.g. U.S. patents Nos. 4,152,231; 4,163,764; 4,391,949 and 4,444,953.

U.S. patent No. 4,152,231 disclosed a cured polymer composition possessing attractive cohesive strength at high temperature, prepared by the radiation curing of a polymer composition in an inert atmosphere, the polymer composition comprising:

- (a) 100 parts by weight of a linear or radial conjugated diene polymer selected from the group consisting of homopolymers of C_4-C_{12} conjugated dienes, and the hydrogenated derivatives thereof;
- (b) from 0 to about 250 parts by weight of a tackifying resin; and

- 2 -

(c) from about 1 to about 100 parts by weight of a di- or tetra-functional acrylate or methacrylate selected from the group consisting of the acrylic and methacrylic acid esters of polyols.

5 The polymers to be used as component (a) were taught in column 5 to be preferably consisting of a nucleus of a coupling agent or residue and a number of arms of substantially linear unsaturated polymers extending outwardly therefrom, the number of arms varying between 2 and 30 and preferably between from about 7 to about 15.

10 Star-shaped block copolymers to be applied could be represented by the formulae $A-X(A)_n$ and $(AB)-X-(B-A)_n$, wherein n was an integer usually between 2 and 30 and wherein X was a coupling agent nucleus, preferably being a poly(vinylaromatic coupling agent) nucleus and more preferably a poly(divinyl benzene) nucleus.

15 According to column 6 of said patent (lines 33-38) star polymers to be used should have peak molecular weights between about 25,000 and 1,250,000 and preferably between 100,000 and 500,000, as determined by gel permeation chromatography (GPC) on a polystyrene scale (apparent mol weights).

20 In column 7, line 55 f.f. the di- to tetrafunctional acrylate or methacrylate coupling agent, which should promote cross-linking of the base polymer during exposure to radiation were clearly regarded as essential component in the adhesive composition, which
25 could be cured by exposure to high energy radiation such as electron beam radiation or ultraviolet radiation.

In column 9, lines 3-11, the amount of required radiation was indicated to be in the range of from 1 to 20 megarads and preferably from about 2 megarad to about 10 megarads for electron
30 beam radiation, whereas for UV radiation as suitable doses are mentioned those received by a 1.5 mil thick adhesive passing under a medium pressure mercury lamp rated at 200 Watts per inch at line speeds of about 10 to about 800 feet per minute and preferably from 25 to 400 feet per minute.

- 3 -

U.S. patent No. 4,163,764 disclosed a process for the preparation of a coupled block copolymer to be used in adhesive compositions, which process comprises the steps of polymerizing a first monomer selected from monovinyl aromatic hydrocarbons under solution polymerization conditions, employing a hydrocarbon diluent, and a first effective increment of a hydrocarbyl monolithium initiator.

Subsequently to the still-living polymerization mixture resulting therefrom at least one second monomer, selected from conjugated dienes together with a second effective increment of a hydrocarbyllithium initiator were added, provided that second initiator increment is greater than said first initiator increment, and the polymerization was continued.

Thereafter, the resulting polymerization admixture was treated with an effective amount of a coupling agent which was at least difunctional, whereby a mixture of coupled block copolymers were produced, which did not contain one predominantly occurring block copolymer, as will be appreciated from column 7, lines 63-68 and column 8, lines 20-65.

It will be appreciated by a person skilled in the art that said U.S. patent did not contain any teaching to radiation curable adhesive compositions and in particular not to any enhancement of the sensitivity of a constituting block copolymer to UV or EB radiation curing.

Moreover, according to the table in the top of columns 7 and 8 the vinyl contents of the polybutadiene blocks in the initially prepared living block copolymers were < 9%, due to the intentional measures specified in column 2, lines 48-63.

From the interrelated U.S. patents Nos. 4,391,949 and 4,444,953 block copolymers and their particular utility in adhesive compositions were known. In particular block copolymers such as KRATON D-1320X are described therein.

The block copolymers showed the structure $(A-B)_x Y(C)_z$, wherein A was a poly(monoalkenyl)aromatic block, B and C were

- 4 -

poly(conjugated diene) polymer blocks, Y was the residue of a multifunctional coupling agent and x plus z was greater than 6.

5 Again no teaching to a person skilled in the art could be found as to radiation curable adhesive compositions and more in particular an enhancement in sensitivity to UV or EB radiation curing of the block copolymer ingredient.

10 On the other hand there was a general teaching during several years to a person skilled in the art that block copolymers to be used in adhesive compositions, curable by radiation, preferably should contain polyisoprene midblocks, with reference to the difficult control of the processability in hot melt adhesive compositions of poly(butadiene) containing block copolymers.

15 In connection therewith the up to now only commercially available radiation sensitive styrenic block copolymer had a polyisoprene midblock (KRATON D-1320X).

Hot melt and solvent based adhesive compositions, containing such SIS block copolymers or structurally similar midblock copolymers and being curable by radiation, were disclosed for example in J.R. Erickson, EB Curable Rubber Has More Heat and Solvent Resistance, Adhesive Age, April 1986, p. 22-24; D. de Jager et al., Les Elastomères Thermoplastiques à base de copolymers blocs styréniques et leur utilisation dans les adhésifs thermofusibles, Groupement de Promotion pour la Connaissance des Plastiques, presented November 1989; J.R. Erickson, Experimental Thermoplastic Rubbers for Enhanced Radiation Crosslinking of Hot Melt PSA's, Hot Melt Symposium, May 1985, TAPPI, Technology Park/Atlanta pages 1, 5 and 6; E.E. Ewins and J.R. Erickson, Formulating to Enhance the Radiation Cross-linking of Thermoplastic Rubber for Hot Melt PSA's, June 1987, Hot Melt Symposium TAPPI, Atlanta, p. 35-49; E.E. Ewins and J.R. Erickson, Pressure Sensitive Adhesives, Formulating to Enhance the Radiation Crosslinking of thermoplastic rubber for hot - melt pressure - sensitive adhesives, Tappi Journal, June 1988, p. 155-158 (presented at 1987 Hot Melt Symposium and 1987 Polymers, Laminations and Coating Conference); and D. de Jager, Developments in Styrenic block copolymers and systems for Hot Melt Pressure

20
25
30
35

- 5 -

Sensitive Adhesives, 15. Münchner Klebstoff-u Veredlungseminar 1990, p. 96-101 and especially p. 97-99.

As general teaching could be derived by a person skilled in the art from these hereinbefore mentioned publications, that
5 radiation curable adhesive compositions had to contain as main ingredient block copolymers derived from styrene and a branched conjugated diene such as isoprene, that for chemically cross-linking in a desired cross-linking density at economical radiation doses by exposure to either electron beam (EB) radiation
10 or UV radiation, the adhesive formulation had to contain at least one supplemental multifunctional coupling agent such as was known from e.g. Radiation Curing of PSA's based on Thermoplastic Rubbers, D.J. St. Clair, Adhesives Age, March 1990, p. 30-35 and in particular p. 35, and that the selection of tackifying resins was
15 considered to be of prime importance for obtaining the maximum amount of polymer cross-linking with a minimum of EB radiation.

Efforts to meet the major challenge in the design of radiation cross-linkable multiblock copolymers suitable for PSA applications of balancing the cohesive and adhesive strength properties of the
20 PSA after irradiation, in an alternative direction were disclosed in e.g. U.S. patent No. 5,066,728.

In particular said patent disclosed a block copolymer to be used in radiation curable adhesive compositions, having endblocks of phenylbutadiene and an elastomeric midblock of a conjugated
25 diene selected from polyisoprene or polybutadiene, giving rise to cross-link later on by radiation, confined primarily to the end-block domains.

The use of phenylbutadiene as the endblock monomer is alleged to solve a key problem of the prior art, namely preferential
30 cross-linking of the endblocks without substantially cross-linking the elastomeric midblocks. Therefore a person skilled in the art in charge of improving the sensitivity of block copolymers relating to radiation curing in adhesive compositions was only led away from the more conventional block copolymer structures.

- 6 -

It will be appreciated that due to higher environmental and economical requirements to be met by coating, sealant, adhesive compositions, comprising block copolymers of vinylaromatic and conjugated diene, and more particularly those radiation curable coating, sealant, adhesive compositions by minimizing the radiation dosage allowing an increase in line speeds and production rates or using weaker radiation, enhancing safety and decreasing environment charging, there is still an aim at developing improved coating, sealant, adhesive compositions and in particular those comprising block copolymers having a relatively simple structure and therefore relatively low manufacturing costs, and in particular those block copolymers which show an improved sensitiveness for UV or EB radiation when included in coating, sealant, adhesive compositions in combination with an attractive melt viscosity in order to reach the most preferred hot melt compositions.

As a result of extensive research and experimentation there were now surprisingly found novel block copolymers, which appeared to have the above mentioned properties aimed at, when included in radiation curable coating, sealing and adhesive compositions and more in particular a pressure sensitive adhesive composition and more particular a pressure sensitive hot melt adhesive composition.

Accordingly, one aspect of the present invention provides novel block copolymers $(AB)_p(B)_qX$ wherein A is a poly(vinylaromatic) block and B is a poly(butadiene) block, wherein X is the residue of a polyvalent coupling agent, wherein p has a number average value of at least 1.5 and q has a number average value of 0 or higher, the sum of the p and q values being at least 4, the block copolymer having an average bound vinylaromatic content in the range of from 7 to 35 wt% and preferably in the range of from 10 to 20 wt%, and having a total apparent molecular weight in the range of from 50,000 to 1,500,000 and wherein the vinyl content in the poly(butadiene) blocks is in the range of from 35 to 70% and preferably from 45 to 70%.

It will be appreciated that the specified values of p and q have to be regarded as number average values, due to the occurrence

- 7 -

of a mixture of a series of individual molecules as obtained according to the hereinafter specified preparation methods.

For example, in case of a ratio between the initially prepared living polymers AB-Li and B-Li of about 1.0 and a tetravalent coupling agent, the individual molecules in the polymer mixture will be $(AB)_4X$, $(AB)_3BX$, $(AB)_2(B)_2X$, $(AB)(B)_3X$, $(B)_4X$ while $(AB)_2(B)_2X$ occurs in an amount of 37.5% (6/16).

The poly(monovinylaromatic) blocks may be derived from styrene, alphasethyl styrene, tert.-butyl styrene, 4-propyl styrene, paramethyl styrene and other ringalkylated styrenes, 1-vinylnaphtalene, 2-vinylnaphtalene as well as mixtures thereof, of which styrene is particularly preferred as main component.

The preferred monomer styrene is most preferably used as pure monomer.

A preferred class of block copolymers according to the present invention will contain B blocks, having an apparent molecular weight in the range of from 15,000 to 250,000 and preferably from 25,000 to 80,000, whereas the A blocks have an apparent molecular weight in the range of from 5,000 to 125,000, preferably from 7,000 to 50,000 and most preferably from 9,000 to 12,000.

The most preferred group of block copolymers to be used in hot melt pressure sensitive adhesive, coating or sealant compositions, can be characterized by a structure $(AB)_p(B)_qX$, wherein X is the residue of a tetravalent coupling agent, wherein p and q both have a number average value in the range from 2.5 to 1.5 whereas the sum of p and q values being 4, and wherein preferably p and q both have a number average value of from 2.1 to 1.9.

The total apparent molecular weight of these block copolymers is in the range of from 50,000 to 350,000 and preferably in the range of from 200,000 to 300,000 and the vinyl content in the poly(butadiene)blocks is in the range of from 35 to 70% and more preferably from 45 to 70%.

The most preferred group of coupled radial block copolymers can be prepared by a process which comprises:

- 2 -

- (a) polymerizing predominantly butadiene in the presence of a living poly(monovinylaromatic) lithium compound A-Li, in which A represents a polymerized monovinyl aromatic block, in the presence of a modifier, so as to form a block copolymer A-B-Li, in which block B substantially comprises 1,2-polymerized butadiene;
- (b) polymerizing predominantly butadiene in the presence of an organolithium initiator, RLi, wherein R being an alkyl group and in the presence of a modifier, so as to form a polymer block B-Li, substantially comprising 1,2-polymerized butadiene molecules, and the molar ratio U between the initiator R-Li and the compound A-Li being in the range of from 0.875 to 1.125 and preferably from 0.95 to 1.05, most preferably the ratio aimed at will be as near as possible to 1.0.
- (c) coupling the mixture of living polymer blocks A-B-Li and B-Li obtained by the polymerizations mentioned under sub (a) and (b) with a coupling agent X which is tetrafunctional.

It will be appreciated that during the polymerization of predominantly butadiene in both steps (a) and (b), a modifier is present, which causes increased vinyl contents (35-70%). Such vinyl contents in the specified range (35 to 70%) were found to increase the EB and/or the UV radiation sensitivity of the final composition.

Modifiers to be suitably used for this purpose can be selected from the group consisting of ethers, amines and other Lewis bases and more in particular from the group consisting of dialkyl ethers of glycols. Most preferred modifiers are selected from dialkyl ether of ethylene glycol, containing the same of different terminal alkoxy groups and optionally bearing an alkyl substituent on the middle ethylene radical, such as monoglyme, diglyme, diethoxy ethane, 1-ethoxy, 2-tert.-butoxy ethane and the like.

As suitable organolithium initiators can be used one or more compounds selected from the group consisting of ethyllithium, n-propyllithium, isopropyllithium, n-butyllithium, sec-butyllithium, tert.-octyllithium, n-decylolithium,

n-eicosyllithium, phenyllithium, 2-naphthyllithium, 4-butylphenyllithium, cyclohexyllithium, 4-cyclopentylbutyllithium and the like, of which sec-butyllithium or tert.-butyllithium are preferred.

5 With the term "predominantly butadiene" as used throughout the present specification is meant that also butadiene, which contains small amounts of other conjugated dienes or vinylaromatic monomers (< 5 wt%) may be used for the beforedescribed polymerization steps.

10 An essential feature of the preparation of said most preferred coupled block copolymer is formed by the aim to obtain a reactive molecular structure, which is stable under processing conditions.

In order to obtain an exact as possible ratio 50/50 of polybutadiene and poly(vinylaromatic) - poly(butadiene) arms, care has to be taken that exactly the same amount of the organolithium
15 compound (eg. s-butyllithium) for the initiation of the polymerization of vinylaromatic (styrene) and of butadiene respectively is added in order to reach an almost equal amount of living polymer chains of both types A-B-Li and B-Li.

20 As coupling agent to form the finally desired star-shaped block copolymer composition, containing $(AB)_2B_2X$, any compound having four almost equally reactive sites can be used. Preferably $SiCl_4$, $SnCl_4$ or DEAP or mixtures thereof can be used.

It will be appreciated that another group of coupled radial block copolymers, showing the improved EB or UV radiation
25 sensitivity according to the invention can be advantageously used in solution pressure sensitive adhesives, coatings and sealings, which can be characterized by a molecular structure $(AB)_p(B)_qX$, wherein A and B are as defined hereinbefore, wherein X is the residue of a polyvalent coupling agent, wherein p has a number
30 average value of at least 1.5 and preferably in the range of from 3 to 20 and more preferably in the range from 3 to 10, wherein q has a number average value of 0 or higher and preferably in the range from 0 to 10, wherein the sum of p and q values being at least 4 and preferably more than 6 and more preferably in the range from 6
35 to 20, and wherein the ratio $p/(p+q)$ is 0.375 or more.

- 10 -

Said group of coupled, radial block copolymers can be prepared by a process which comprises:

- 5 (a) polymerizing predominantly butadiene in the presence of a living poly(monovinyl aromatic) lithium compound A-Li, in which A represents a polymerized monovinyl arene block, in the presence of a modifier, so as to form a block copolymer A-B-Li, in which block B substantially comprises 1,2-polymerized butadiene;
- 10 (b) optionally polymerizing predominantly butadiene in the presence of an organolithium initiator RLi, wherein R being an alkyl group and in the presence of a modifier, so as to form a polymer block B-Li, substantially comprising 1,2-polymerized butadiene molecules, and wherein the molar ratio U between the initiator R-Li and the compound A-Li is rather irrelevant;
- 15 (c) coupling the living polymers AB-Li, optionally mixed with living polymers B-Li with a polyfunctional coupling agent X, whereof the functionality is at least 4 and preferably in the range of from 4 to 20 and more preferably from 6 to 20.

20 A more preferred subgroup of such coupled radial block copolymers is formed by a process which comprises both steps (a) and (b) as hereinbefore defined.

The advantages obtained by application of the hereinbefore specified groups of block copolymers according to the present invention are:

- 25 (a) improved EB or UV radiation sensitivity as compared to the conventional, generally applied prior art block copolymers, like KRATON D-1320X, which means that less radiation energy per surface units is needed or higher processing speed and larger production volumes may be possible;
- 30 (b) improved high temperature resistance is obtained after curing of the adhesive composition, comprising the block copolymer;
- (c) no additional separate cross-linking agents like acrylates etc. have been found to be necessary, which means significantly less danger for environment and human health (toxicity of adhesive composition); in combination with
- 35

(d) simple structure of the block copolymer which can be manufactured with a coupling efficiency of greater than 95% in usual relatively simple equipment giving rise to a rather cheap block copolymer of a well-regulated structure.

5 It will be appreciated that another aspect of the present invention will be formed by solution and hot melt adhesive compositions. A preferred aspect is formed by hot melt adhesive compositions, having an improved sensitivity to UV and/or EB radiation curing comprising as main ingredient the hereinbefore
10 specified coupled block copolymers $(AB)_p(B)_qX$, together with the usual ingredients of pressure sensitive adhesive compositions, such as tackifying resin, extender oil and/or plasticizer, petroleum derived waxes, antioxidant, photosensitizer (only necessary in case of UV radiation curing) and optionally an A block modifying resin.

15 It will be appreciated that another aspect of the present invention is formed by solution adhesive compositions, comprising the block copolymers as specified in pages 6 and 7.

The block copolymer by itself has appeared to be not sufficiently tacky or sticky. Therefore it is necessary to add a
20 tackifying resin that is compatible with the elastomeric poly-(butadiene) blocks.

In the adhesive compositions according to the present invention it has been found preferable that the tackifying resin should have a low level of unsaturation in order to achieve low
25 radiation curing dosage of the adhesive composition; mixtures of resins having higher and lower unsaturations and softening points may also be used but are less preferred due to possible uncontrollable side reactions.

30 Examples of resins which are useful in the adhesive compositions of the present invention include saturated resins, esters of resins, polyterpenes, terpene phenol resins, and polymerized mixed olefins or mixtures thereof.

The amount of tackifying resin or resins in total varies from 0 to 500 parts per hundred parts of block copolymer (phr),
35 preferably from 50 to 200 phr.

- 12 -

Optionally a modifying resin that is compatible with the poly(vinyl aromatic) blocks, may be added as long as it does not appreciably hinder the radiation curing process as a result of mixing on a molecular level with the poly(butadiene) blocks.

5 Compatibility is judged by the method disclosed in U.S. patent No. 3,917,607. Normally the resin should have a softening point above 100 °C as determined by ASTM method E28.

The tackifiers are selected for their ability to tackify the elastomeric block and their compatibility therewith.

10 However, in the present invention, it is preferable that the tackifying resin has a low level of unsaturation in order to achieve low dosage radiation curing of the composition. Mixtures of resins having higher and lower unsaturations and softening points may also be used. Examples of resins which are useful in the
15 compositions of this invention include unsaturated and hydrogenated resins, esters of resins, polyterpenes, terpene phenol resins, and polymerised mixed olefins with hydrogenated resins preferred.

Examples of useful tackifying resins are ESCOREZ 5300 series (ESCOREZ is a trade mark); REGALITE R91, R101, S100, S260 (REGALITE
20 is a trade mark); REGALREZ 1018, 3102, 6108, 5095 (REGALREZ is a trade mark); ZONATAC Lite series like the ZONATAC 105 Lite (ZONATAC is a trade mark); and the like.

The adhesive compositions of the instant invention may also contain plasticisers such as rubber extending or compounding oils
25 in order to provide wetting action and/or viscosity control. These plasticisers are well-known in the art and may include both high saturated content oils and high aromatic content oils. Said plasticizers include not only the usual plasticizers but also embrace the use of olefin oligomers and low molecular weight
30 polymers as well as vegetable and animal oil and their derivatives. The petroleum derived oils which may be employed are relatively high boiling materials and preferably contain only a minor proportion of aromatic hydrocarbons (preferably less than 30 percent and, more preferably, less than 15 percent by weight of
35 the oil).

Such oils are for example SHELLFLEX 451, 4510 (SHELLFLEX is a trade mark); ONDINA 68 (ONDINA is a trade mark); RISELLA 68 (RISELLA is a trade mark); PRIMOL 352 (PRIMOL is a trade mark); WITCO 260 (WITCO is a trade mark); and the like.

5 Alternatively, the oil may be totally non-aromatic. The oligomers may be polypropylene, polybutene, hydrogenated polyisoprene, hydrogenated polybutadiene, or the like having average weights preferably between 200 and about 10,000.

10 Vegetable and animal oils include glyceryl esters of usual fatty acids and polymerisation products thereof.

The amount of plasticiser and oil employed varies from 0 to 500 phr (parts by weight per hundred parts by weight of rubber), preferably from 0 to 100 phr and more preferably from 5 to 60 phr.

15 Various petroleum derived waxes may also be present in the composition in order to impart fluidity in the molten condition of the adhesive and flexibility to the set adhesive, and to serve as a wetting agent for bonding cellulosic fibers. The term "petroleum derived wax" includes both paraffin and microcrystalline waxes having a melting point within the range of about 54 °C to about 20 107 °C as well as synthetic waxes such as low molecular weight polyethylene or Fisher-Tropsch waxes.

The amount of petroleum derived waxes employed herein varies from 0 to about 100 phr, preferably from 0 to about 15 phr.

25 It will be appreciated that the best results (i.e. a satisfactory curve achieved with minimum irradiation dosage) are achieved when, like the tackifying resins, the plasticisers and oils contain low levels of unsaturation. Additionally, it is also preferable to minimize the aromatic content thereof.

30 The adhesive compositions may further contain conventional additives such as e.g. stabilisers, pigments, fillers and the like but the compositions should be free of other additives and impurities which adversely affect the adhesive properties of the composition, and particularly the high temperature properties thereof.

- 14 -

Stabilisers and oxidation inhibitors are typically added to the commercially available compounds in order to protect the ingredients against degradation during preparation and use of the adhesive compositions, however without interfering with the irradiation curing of the polymer.

Combinations of stabilisers are often more effective due to the different mechanisms of degradation to which various polymers are subject.

Certain hindered phenols, organo-metallic compounds, aromatic amines, aromatic phosphites and sulphur compounds are useful for this purpose.

Examples of effective types of these materials include phenolic antioxidants, thio compounds and tris-(nonylated phenyl) phosphites.

Examples of commercially available antioxidants are "IRGANOX 565" 2,4-bis-(n-octylthio)-6-(4-hydroxy-3,5-di-tertiary-butyl anilino)-1,3,5-triazine, "IONOL" 2,6-di-tertiary-butyl-4-methyl phenol, "IRGANOX 1010" tetrakis-ethylene-(3,5-di-tertiary-butyl-4-hydroxy-hydrocinnamate)methane, "IONOX 330" 3,4,6-tris (3,5-di-tertiary-butyl-p-hydroxybenzyl)-1,3,5-trimethylbenzene and "POLYGARD HR" tris-(2,4-di-tertiary-butyl-phenyl) phosphite.

In general from about 0.01 percent to about 5.0 percent by weight of one or more antioxidants is included in the adhesive composition.

The adhesive compositions of the present invention may be prepared by blending block copolymers, tackifying resins and other desired ingredients at an elevated temperature, e.g. at about 160 °C (hot-melt) using a Z blade mixer or extruder or any other usual type of mixer for that propose.

Adhesives of the present invention are especially suited for preparation as 100% solids hot-melt adhesives since they give relatively low processing viscosities, less than hundred thousand centipoise, and adequate pot life, up to several hours, at processing temperature of about 150 °C to 180 °C. A preferred method for processing is the use of an extruder to mix the adhesive

- 15 -

and feed the coating die as is disclosed in US patent No. 3,984,509.

The compositions of the present invention are cured by exposure to high energy ionizing radiation such as electron beam radiation.

The electron beam radiation or high energy ionizing radiation which employed to effect the cross-linking reaction can be obtained from any suitable source such as an atomic pile, an electron gun, a resonant transformer accelerator, a Van de Graaf electron accelerator, a Lineac electron accelerator, a betatron, a synchrotron, a cyclotron, or the like. Radiation from these sources will produce ionizing radiation such as electrons, protons, neutrons, deuterons, gamma rays, X rays, alpha particles, and beta particles.

The cross-linking reaction is conveniently effected at room temperature, but it can be conducted at depressed or elevated temperatures if desired. It is also within the spirit and scope of the invention to effect the cross-linking reaction within the confines of an inert atmosphere to prevent interference in the block copolymer cross-linking, particularly at an exposed surface.

Additionally, cross-linking may be effected by irradiating the composition which is sandwiched between substrates such as when the composition is utilized as a tie-layer between these substrates. Similarly, when the cross-linking reaction is not conducted within the confines of an inert atmosphere, release paper may be placed over the exposed composition surface contacting and covering same. Thus, the composition may be cross-linked by irradiation through the release paper or to the substrate.

The amount of irradiation required to produce a satisfactory cure depends primarily upon the type and concentration of the block copolymer employed and the unsaturation level present in the composition. Suitable dosages of electron beam irradiation are in the range from 0.5 to 7 Mrad, preferably about 1 Mrad to about 6 Mrad and more preferably about 1 Mrad to about 3 Mrad.

- 16 -

The adhesive compositions may also be cured by exposure to ultraviolet radiation for a period of time sufficient to effect the desired amount of cross-linking. Ordinarily, when use of ultraviolet light is contemplated the adhesive composition will be formulated with from 0.2 to 5% of an ultraviolet sensitizing component (photo-initiator) based on the weight of the adhesive. Any of the known ultraviolet sensitizing compounds may be used.

Useful photo-initiators are 2,2-dimethoxy-2 phenyl acetophenone, benzophenone, propiophenone, cyclopropyl phenyl ketone, acetophenone, 1,3,5-triacetyl benzene, benzaldehyde, thioxanthane, anthraquinone, beta-naphtyl phenyl ketone, beta-naphthaldehyde, beta-acetonaphthone; 2,3-pentanedione, benzil, fluoronone, pyrene, benzanthrone, anthracene and the class arylketones substituted with morpholino and with hydrocarbyl thio groups such as disclosed in US patent No. 4,582,862.

A photo-initiator such as IRGACURE 651 or IRGACURE 907 (tradename of Ciba-Geigy) is preferred.

It will be appreciated that the length of exposure will be dependent on the intensity of the radiation, the amount and particular type of the ultraviolet sensitizing compound employed, thickness of the adhesive layer etc. The photo-initiators may preferably be included in an amount in the range of from 0.5 to 5 parts by weight per 100 parts by weight of block copolymer and preferably in an amount in the range of from 1 to 4 parts by weight.

A preferred use of the present formulation is in the preparation of pressure-sensitive adhesive (PSA) tapes or in the manufacture of labels. The pressure-sensitive adhesive tape comprises a flexible backing sheet and a layer of the adhesive composition of the instant invention coated on one major surface of the backing sheet. The backing sheet may be a plastic film, paper or any other suitable material and the tape may include various other layers or coatings, such as primers, release coatings and the like, which are used in the manufacture of pressure-sensitive adhesive tapes.

- 17 -

The invention is further illustrated by means of the following examples, however, without restricting the scope of the invention to these preferred embodiments.

Preparation of branched block copolymers (I-XII)

5 To a first 5 l reactor about 3 l of cyclohexane were added, which was stripped during about half an hour with nitrogen. After addition of 150 g of styrene, the reactor contents were titrated at room temperature with a 12 wt% solution of sec.butyllithium (BuLi) in cyclohexane, whereby any impurities present in the reactor
10 mixture were scavenged. Hereafter 15.6 mmol BuLi were added and the temperature was raised to and maintained at 50 °C. After about 30 minutes the poly(styrene) Li block had been formed and the contents were transferred to a second 10 l reactor, which had previously been charged with about 3 l of cyclohexane being
15 stripped with nitrogen during about half an hour and a varying amount of diethoxy ethane modifier and 350 g of butadiene which had previously been titrated with a butyllithium solution.

The temperature was raised to 50 °C. A predetermined additional amount of BuLi was added to the second reactor in
20 varying amounts and an amount of 500 g of butadiene was gradually dosed over about 30 minutes.

Thereafter the second reactor was brought to and kept at 80 °C, 7.7 mmoles of SiCl_4 were added and the coupling reaction was performed in about 30 minutes.

25 After about 2 hours 10 g of 2,6-di-tert.-butyl-4-methylphenol were added. Hereafter the solvent was removed by steam stripping and the obtained polymer was dried in an oven at 60 °C during 5-6 hours.

The obtained branched block copolymers are listed in the
30 following Table I:

Table 1

reactor 1 reactor 2

Ex.	cyclo- hexane	styrene (g)	BuLi (mmol)	cyclo- hexane (kg)	butadiene batch (g)	diethoxy ethane (ppm)	BuLi (mmol)	buta- diene dose	SiCl ₄ (mmol)	vinyl cont. (%)	perc. SB areas (%)
I	2.41	152	15.6	2.41	350	0	15.6	500	7.7	8	50
II	2.34	150	14.9	2.34	350	60	13.9	500	7.1	31	50
III	2.34	150	14.3	2.34	350	75	13.3	500	7.1	42	50
IV	2.34	150	14.1	2.34	350	150	13.1	500	7.8	59	50
V	2.34	150	13.6	2.34	350	225	13.0	500	7.8	68	50
VI	2.34	130	12.5	2.34	350	150	22.8	820	7.8	62	35

In about the same way as described hereinbefore block copolymers were prepared as listed in the following

Table 2:

reactor 1				reactor 2								
Ex.	cyclo- hexane (kg)	styrene (g)	RuI ₂ (mmol)	cyclo- hexane (kg)	buta- diene batch (kg)	diethoxy ethane (ppm)	RuI ₂ (mmol)	buta- diene dose (mmol)	coupling agent	vinyl cont. (%)	perc. SB arms (%)	coupling efficiency (%)
VII	2.35	100	9.1	2.35	350	250	4.5	550	SiCl ₄ (4.4)	62	70	90
VIII	2.35	100	9.3	2.35	350	250	11.8	550	SiCl ₄ (6.1)	60	50	93
IX	2.35	100	11.1	2.35	350	250	-	550	SiCl ₄ (3.5)	63	100	85
X	2.34	100	9.5	2.34	350	250	-	550	DVB (38.1)	63	100	87
XI	2.34	100	10.3	2.34	350	250	12.9	550	DVB (41.2)	62	50	96
XII	2.34	100	9.6	2.35	350	250	4.8	550	DVB (38.4)	63	70	91

Estimation of properties:

5 The hot-melt viscosity of an adhesive formulation containing the listed polymers was measured, as listed hereinafter in Tables 3 and 4 in comparison to that one of KRATON D-1320X block copolymer, which was up to now preferably used in similarly composed radiation curable adhesive compositions.

The adhesive composition used was composed as follows:

Block copolymer	100 pts
FORAL 85	90 phr
IRGANOX 1010	1 phr

Table 3

Polymer	Hot-melt viscosity at 180 °C	Hot-melt viscosity after 3 hours at 180 °C
	(Pa.s)	(Pa.s)
I	115	120
II	53	75
III	75	105
IV	52	70
V	40	40
VI	117	320
KRATON D-1320X	200	380

- 21 -

Table 4

Melt viscosity *

Pa.s

Polymer code	Pa.s	
	after 30 min.	after 180 min.
XI	338	> 2000
XII	1900	> 2000
X	> 2000	> 2000
VIII	127	299
VII	828	> 2000
IX	1690	> 2000
D1320X	112	125

* The adhesive formulation used for melt viscosity measurement was composed

100 pts polymer

90 phr FORAL 85 (tradename)

15 phr SHELLFLEX 451 (tradename)

2 phr IRGANOX 1010 (tradename)

and the viscosity was measured with BROOKFIELD THERMOSEL (tradename).

5 Most of these polymers were found to be very stable under processing conditions, the stability improving with the increasing vinyl content (polymers IV and V were found to be most stable).

The polymers were compounded in adhesive formulations as follows:

10 A radiation sensitive adhesive formulation to provide radiation curing, based on KRATON D-1320X block copolymer, was prepared according to the following recipe:

Block copolymer	100 pts
REGALITE R91	150 phr
REGALREZ 1018	60 phr
IRGACURE 651	3 phr
IRGANOX 1010	1 phr

- 22 -

This formulation was found to provide also very aggressive tack properties.

The polymers varying in vinyl content and having therefore different T_g , were not compounded into the same formulation. The amount of ingredients was adjusted to get the same mid-block T_g than that of the KRATON D-1320 based formulation. However, and because the curing is done in the butadiene mid-block, the butadiene mid-block fraction present in the adhesive was kept constant (otherwise, an adhesive having a higher proportion of butadiene mid-block might be more radiation sensitive than another one).

The Holding power at 95 °C are as follows: (this is a Holding power test carried out at a temperature very close to the polystyrene softening point; it is therefore a very reliable test and unirradiated polymers do not resist longer than few seconds).

The test was performed with 0.5 kg load on a 1 square inch surface after UV curing at 5 m/min under a Fusion D-Bulb. The samples were coated with 22 g/m². The results are given as function of the dosage (or the number of passes) in Table 5:

Table 5

Holding power at 95 °C on 0.5 kg load on 1 square inch after UV curing

	1 Pass (h)	2 Passes (h)
I	0	4.2
II	0.5	0.3
III	3.3	> 280
IV	> 116	> 280
V	> 116	> 280
VI	> 116	> 280
KRATON D-1320X	50	> 280

From previous test results it will be clear that polymers I and II are outside the present invention as claimed hereinafter.

The same test was performed on the samples IV, V and VI, but with a load of 1 kg per square inch. The results are as indicated in Table 6:

5

Table-6

Holding power at 95 °C on 1 kg load on 1 square inch after UV curing

	1 Pass (h)	2 Passes (h)
IV	0.3	> 280
V	106	> 280
VI	> 280	> 280
KRATON D-1320X	0.2	8.6

Polymers I to VI were also compared to KRATON D-1320X by Shear Adhesion Failure Temperature (SAFT) after UV curing. The results are given as function of the dosage in Table 7.

- 24 -

Table 7

	0 Pass (°C)	1 Pass (°C)	2 Passes (°C)
I	80	103	165
II	79	112	180
III	77	128	115
IV	99	> 188	> 185
V	75	> 179	> 185
VI	78	154	> 185
KRATON D-1320 X	77	148	157

Using the following adhesive composition for UV and EB radiation:

Polymer	100	pts
FORAL 85	90	phr
SHELLFLEX 451	15	phr
IRGACURE 651	3	phr
IRGANOX 1010	2	phr

the polymers VII-XII were tested as to SAFT after curing, as listed in the tables 3 and 9.

- 25 -

Table 8

SAFT (°C) after UV curing of adhesive compositions

SAFT, °C		UV-dose, number of passes at 15 m/min				
Polymer code	S-B content %	0	1	2	4	6
XI	50	80	> 200	> 200	> 200	> 200
XII	70	101	> 200	> 200	> 200	> 200
X	100	115	> 200	> 200	> 200	> 200
VIII	50	79	93	> 200	> 200	> 200
VII	70	100	151	> 200	> 200	> 200
IX	100	103	158	> 200	> 200	> 200

Table 9

SAFT (°C) after EB curing of adhesive compositions

		EB-dose, Megarads		
Polymer code	S-B content %	0	1	2
XI	50	80	109	> 200
XII	70	101	> 200	> 200
X	100	115	146	> 200
VIII	50	79	83	85
VII	70	100	113	126
IX	100	103	120	137

- 26 -

It will be appreciated from the previous examples that a significant improvement in radiation sensitivity could be obtained with the polymers of the present invention as compared to KRATON D-1320X.

5 Although some of these polymers e.g. VI, X, XI and XII appear to have high melt viscosities making them inappropriate for hot melt adhesive compositions, they can advantageously be used in solution pressure sensitive adhesive compositions due to their excellent radiation sensitivity.

10 The most preferred type of polymers, which can be used in hot melt adhesive compositions and which show a combination of low melt viscosity and attractive radiation sensitivity is represented by polymers IV and V.

C L A I M S

1. Radiation sensitive block copolymers $(AB)_p(B)_qX$ wherein A is a poly(vinylaromatic) block and B is a poly(butadiene) block, wherein X is the residue of a polyvalent coupling agent, wherein p has a number average value of at least 1.5 and wherein q has a number average value of 0 or higher, the sum of p and q values being at least 4, the block copolymer having an average bound vinylaromatic content in the range of from 7 to 35 wt% and preferably in the range of from 10 to 20 wt%, and having a total apparent molecular weight in the range of from 50,000 to 1,500,000, and wherein the vinyl content in the poly(butadiene) blocks is in the range of from 35 to 70%.
2. Radiation sensitive block copolymers according to claim 1, characterized in that the blocks A are derived from styrene as main component.
3. Radiation sensitive block copolymers, according to claims 1 and 2, characterized in that the B blocks have an apparent molecular weight in the range of from 15,000 to 250,000 and preferably from 25,000 to 80,000 and the A blocks have an apparent molecular weight in the range of from 5,000 to 125,000 and preferably from 7,000 to 50,000 and more preferably from 9,000 to 12,000.
4. Radiation sensitive block copolymers according to claims 1-3, having the structure $(AB)_p(B)_qX$, wherein X is the residue of a tetravalent coupling agent, wherein p and q both have a number average value in the range from 2.5 to 1.5, whereas the sum of p and q values being 4.
5. Radiation sensitive block copolymers according to claim 4, wherein p and q both have a number average value of from 2.1 to 1.9.

6. Radiation sensitive block copolymers according to claims 4 and 5, characterized in that they have a total apparent molecular weight in the range of from 200,000 to 300,000.
7. Radiation sensitive block copolymers according to claims 4-6, characterized in that the vinyl content in the poly(butadiene) blocks is in the range of from 45 to 70%.
8. Radiation sensitive block copolymers according to claims 1-3, characterized in that p has a number average value of at least 1.5 and preferably in the range of from 3 to 20 and more preferably in the range from 3 to 10, wherein q has a number average value of 0 or higher, and preferably in the range from 0 to 10, the sum of p and q values being at least 4 and wherein the ratio of $p/(p+q)$ is 0.375 or more.
9. Radiation sensitive block copolymers according to claim 8, wherein the sum of p and q values is more than 6, and preferably in the range from 6 to 20.
10. Process for the preparation of radiation sensitive block copolymers according to claims 4-7, comprising:
- (a) polymerizing predominantly butadiene in the presence of a living poly(monovinylaromatic)lithium compound A-Li, in which A represents a polymerized monovinylaromatic block, in the presence of a modifier, so as to form a block copolymer AB-Li, in which block B substantially comprises 1,2-polymerized butadiene;
- (b) polymerizing predominantly butadiene in the presence of an organolithium initiator, RLi, wherein R being an alkyl group and in the presence of a modifier, so as to form a polymer block B-Li, substantially comprising 1,2-polymerized butadiene molecules, and the molar ratio u between the initiator R-Li and the compound A-Li being in the range of from 0.90 to 1.10 and preferably from 0.95 to 1.05, most preferably the ratio aimed at will be as near as possible to 1.0;
- (c) coupling the mixture of living polymer blocks A-B-Li and B-Li obtained by the polymerizations mentioned under sub (a) and (b) with a coupling agent X which is tetrafunctional.

11. Process according to claim 10, characterized in that exactly the same amount of the organolithium compound for the initiation of the polymerization of styrene and of butadiene is added.
12. Process according to claims 10 and 11, characterized in that
5 as coupling agent SiCl_4 , SnCl_4 or DEAP or mixtures thereof are used.
13. Radiation curable sealant, coating or adhesive compositions, comprising as main ingredient one or more block copolymers according to claims 1-9.
- 10 14. Radiation curable adhesive compositions, comprising one or more block copolymers according to claims 1-9 in addition to one or more usual ingredients such as tackifying resin, extender oil, plasticizer, petroleum derived waxes, antioxidant, photosensitizer and a poly(vinylaromatic) block modifying resin.
- 15 15. Radiation curable hot melt adhesive compositions characterized in that they comprise one or more of the block copolymers according to claims 4-7.
16. Radiation curable solution adhesive compositions characterized in that they comprise one or more of the block copolymers according
20 to claims 8 and 9.
17. UV radiation curable adhesive compositions, comprising in addition to one or more block copolymers according to claims 1-9, at least one photo-initiator selected from 2,2 dimethoxy-2-phenyl acetophenone, benzophenone, propiophenone, cyclopropyl phenyl
25 ketone, acetophenone; 1,3,5-triacetyl benzene, benzaldehyde, thioxanthane, anthraquinone, beta naphthyl phenyl ketone, beta naphthaldehyde, beta-acetonaphthone, 2,3-pentanedione, benzil, fluoronone, pyrene, benzanthrone, anthracene and the class arylketones substituted with morpholino and with hydrocarbyl thio
30 groups.
18. UV radiation curable adhesive compositions according to claim 17, comprising IRGACURE 651 or IRGACURE 907 as photo-initiator.
19. UV radiation curable adhesive compositions according to
35 claims 17 and 18, characterized in that the photo-initiator has

- 30 -

been included in an amount in the range of from 0.5 to 5 parts by weight per 100 parts by weight of block copolymer and preferably in the range of from 1 to 4 parts by weight.

5. 20. Pressure sensitive curable tapes or labels, comprising a flexible backing sheet and a layer of the adhesive composition according to claims 13-19, coated on one major surface of the backing sheet.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 93/01407

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)⁶
According to International Patent Classification (IPC) or to both National Classification and IPC
Int.Cl. 5 C08F297/04; C09J153/02; C09D153/02; C08G81/02

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System

Classification Symbols

Int.Cl. 5

C08F ;

C09J ;

C09D ;

C08G

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	US,A,4 092 375 (VREUGDENHIL) 30 May 1978 see abstract see claim 1; table ---	1-12
X	US,A,4 163 764 (NASH) 7 August 1979 see claims 1,8,9,16,18,20 ---	1,2,4,5
Y	EP,A,0 008 146 (SHELL INTERNATIONALE RESEARCH) 20 February 1980 see page 4, line 14 - line 23 see page 7, line 25 - line 32 see page 8, line 3 - line 8 ---	1-6, 13-20
	--- -/-	

* Special categories of cited documents: ¹⁰

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"T" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"A" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

06 AUGUST 1993

Date of Mailing of this International Search Report

25.08.93

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

LOISELET-TAISNE S.

II. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category*	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
Y	WO,A,8 809 800 (AVERY INTERNATIONAL CORP.) 15 December 1988 see page 5, line 9 - line 14; claim 16 see page 12, line 14 - line 15 ---	1-6, 13-20
A	EP,A,0 368 141 (FULLER H B CO.) 16 May 1990 see page 4, line 42 - page 5, line 7; claim 1 ----	1,20
A	US,A,5 066 728 (AUDET) 19 November 1991 see column 3 lines 21,39,47,58 -----	1

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

EP 9301407
SA 74843

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for those particulars which are merely given for the purpose of information. 06/08/93

Patent document cited in search report	Publication date	Patent family number(s)	Publication date
US-A-4092375	30-05-78	None	
US-A-4163764	07-08-79	AU-B- 519845	24-12-81
		AU-A- 3713178	20-12-79
		BE-A- 868373	22-12-78
		CA-A- 1120636	23-03-82
EP-A-0008146	20-02-80	US-A- 4151057	24-04-79
		AT-T- 3051	15-04-83
		AU-B- 528364	28-04-83
		AU-A- 4980179	21-02-80
		CA-A- 1126688	29-06-82
		JP-A- 1236261	21-09-89
		JP-C- 1626174	28-11-91
		JP-B- 2042846	26-09-90
		JP-B- 1038147	11-08-89
		JP-C- 1554574	23-04-90
		JP-A- 55025494	23-02-80
WO-A-8809800	15-12-88	US-A- 4948825	14-08-90
		AU-A- 1947388	04-01-89
		EP-A- 0316435	24-05-89
		JP-T- 2500198	25-01-90
		US-A- 5093406	03-03-92
		US-A- 5135978	04-08-92
		US-A- 5115008	19-05-92
EP-A-0368141	16-05-90	US-A- 5024667	18-06-91
		CA-A- 2002358	07-05-90
		JP-A- 2232049	14-09-90
		US-A- 5057571	15-10-91
US-A-5066728	19-11-91	WO-A- 9206125	16-04-92
		US-A- 5135816	04-08-92

EP 9301407

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82